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A Comparison of Extraction Techniques
for Polynuclear Aromatic Hydrocarbon Analysis of
Industrial Effluents and Natural Waters

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Running Title: PAH Extraction Method Comparison

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The analysis for polynuclear aromatic hydrocarbons (PAH) is an important activity of environmental laboratories. In analyzing a wide array of environmental samples, the need for a systematic study and comparison of extraction techniques and procedures was strongly indicated. The present paper gives an account of such investigations, using aqueous samples.

Four extraction techniques were evaluated for the analysis of PAH from industrial process streams and effluents, and from natural waters. Manual liquid-liquid (shake-out) extraction, and continuous liquid-liquid extraction were investigated. Also examined were the applications of a modified Likens-Nickerson apparatus which operates on the principle of continuous solvent extraction of the steam distillate, and a micro adsorption column, packed with 10 μm C_{18} reverse phase material.

Organic-free water spiked with PAH, industrial effluent samples and a natural water sample were analyzed for PAH following extraction using these various methods. The extraction procedures and subsequent clean-ups were geared towards high performance liquid chromatographic (HPLC) fluorescence detection.

EXPERIMENTAL

All solvents used were of high purity and the extraction and concentration equipment was thoroughly cleaned prior to use. Samples were analyzed in parallel with blanks. In general, organic-free water and solvents were free from PAH, but occasionally the extraction and concentration apparatus became contaminated. In cases when contamination was detected, the problem was rectified by re-cleaning the glassware.

HPLC

The analytical method for PAH determination utilized HPLC with a C_{18} reverse phase column. The eluent was a mixture of acetonitrile

(75%) and water (25% v/v) applied at a pressure of 105 kg/cm² and a flow rate of 1.0 ml/min. Variable wavelength excitation and emission fluorescence detection were used, as described elsewhere (4) in detail.

SAMPLES

A sufficient quantity of aqueous sample was obtained to ensure that each of the four extraction procedures could be completely evaluated. Generally, a 32-liter sample comprising 8 4-liter bottles was required.

(a) Filtered Samples

After the sample was filtered, the sample bottle was rinsed with organic-free water, and this aqueous washing was filtered. This process was repeated twice. The glass sample bottle was then rinsed with the appropriate organic solvent and the solvent washings were pooled. The aqueous filtrate was also pooled to ensure homogeneity of the dissolved PAH fraction. The dissolved PAH fraction thus consisted of the filtrate extract and the rinsed bottle washings.

(b) Non-filtered Samples

The complete sample from the collection bottle was added to the extraction apparatus, the sample bottle was rinsed twice with organic-free water, and the aqueous washings were added to the sample. The sample bottle was rinsed twice with the appropriate solvent and added to the rest of the solvent used for the particular extraction.

FILTRATION

Half of the sample was filtered through pre-extracted .45 μ m membrane filters. In cases where the particulate matter loading was high, pre-extracted "Celite" was used to aid filtration. Spent filters were Soxhlet extracted for 24 hours with benzene. The extracts were concentrated, by rotary evaporation, to near dryness and made up with acetonitrile-water for HPLC analysis.

CLEAN-UP

When a clean-up procedure was warranted, the extract was chromatographed on pre-extracted, deactivated "Florisil" with cyclohexane, then concentrated and prepared for HPLC analysis.

EXTRACTION PROCEDURES

1. Manual Liquid-Liquid Extraction

To a 1-liter sample in a 2-liter separatory funnel, 25 ml of methylene chloride was added to saturate the solution. The aqueous sample was then extracted once with 100 ml and twice with 50 ml of methylene chloride. The combined extracts were concentrated by rotary evaporation to near dryness and made up with acetonitrile-water for HPLC analysis. When extracting a 4-liter sample, two 2-liter separatory funnels were used in parallel, and the extraction procedure remained the same as with a 1-liter sample.

2. Continuous Liquid-Liquid Extraction

The continuous liquid-liquid extractor was designed specifically for solvents lighter than water. The extractor had a volume of 5 liters and the diffuser tube utilized a coarse glass frit. Generally, 4-liter samples were taken, so the remaining volume was made up with organic-free water. Approximately 250 ml of benzene was used, at a distillation rate of 5 ml/min in the 24 hour extraction procedure. The extract was concentrated to near dryness, and made up with acetonitrile-water for HPLC analysis.

3. Steam Distillation Extraction

Using a modified Likens-Nickerson apparatus (3), 4-liters of sample was steam distilled on a condensor, at a distillation rate of 6 ml/min, and the condensate was continuously extracted with methylene chloride, at an approximate distillation rate of 3 ml/min. After 24

hours, the solvent (250 ml) was concentrated by rotary evaporation to near dryness, then the extract was made up with acetonitrile-water for HPLC analysis. Other types of continuous steam distillation/extraction equipment have been described in the literature (2, 5) and are commercially available.

4. Micro Adsorption Column

Aqueous filtered samples were passed at 4-6 ml/min through a cartridge micro adsorption column (4.6 mm x 10 cm) packed with 10 μ m C₁₈ reverse phase material. The pressures required to achieve the flow-rate were 20-35 kg/cm². At pressures greater than 35 kg/cm² (500 psi), the micro column developed leaks at the cartridge inlet line. The micro column was eluted with 10 ml of acetonitrile, which was concentrated to 1.0 ml for HPLC analysis.

PAH RECOVERY STUDIES

1. ORGANIC-FREE WATER SPIKED WITH PAH

Organic-free water was spiked at concentrations of 2,4,6 and 8 ng/l of individual PAH in acetonitrile. Recoveries for benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DBA), benzo(ghi)perylene (BP) and o-phenylenepyrene (OPP) were excellent, with the exception of the micro adsorption column, as can be seen in Table 1. The percent recoveries are the grand average of the four spike concentrations.

The glass vessels that were used in these spiking experiments were washed with the extracting solvent as part of the normal extraction procedure. An exception to this procedure was the micro column extraction. The original intent was to use the spent micro column in place of the analytical column and elute directly, to the fluorescent detector. However, the resolution of the PAH was poor, so this approach was abandoned. The organics were eluted from the micro column with a small amount of acetonitrile, concentrated and analyzed by HPLC. After all the water had been

TABLE 1

Percent Recovery of PAH from Organic-free Water

Compound	Extraction Technique			
	liquid-liquid	Continuous liquid-liquid	Steam distillation	Adsorption column
BkF	96	93.4	96.1	55.7
BaP	75.7	84.5	94	43.1
DBA	94.1	92.9	88.2	42.2
BP	99.7	88.9	92.6	39.8
OPP	96.7	93.3	89.8	37.1
AVERAGE	92.4	90.6	92.1	43.6

pumped through the micro column, the glass vessel was extracted with methylene chloride. An average recovery of 39.0% was obtained for the 5 PAH in this study, bringing the total average recovery to 82.6%.

There were serious disadvantages to using the micro adsorption column. The flow rate inevitably slowed down with time, possibly because the column became plugged, or the packing material swelled. This extraction technique was abandoned at this stage because the time required to pump 1 to 4 liters through the adsorption column was excessive, the sample container had to be extracted separately, and the overall recovery of the PAH was the poorest of the 4 methods evaluated.

2. STEEL MILL PROCESS STREAM

The steel mill process stream used in this study was a "flushing liquor", which consisted of an aqueous solution of the gases emitted from a coking oven. The suspended solids level in the sample was 50 mg/l, and consisted primarily of flakes of carbon. When the sample was filtered through a .45 μ m membrane filter, oily deposits formed on the filtration equipment, and oily material passed through the filter. This may have resulted in the samples being somewhat non-homogeneous.

As the filtered sample was quite concentrated, a 10 μ l direct aqueous injection was possible. This chromatogram is illustrated in Figure 1. The concentrations of the dissolved PAH obtained by the various extraction techniques are listed in Table 2. The results from each of the methods evaluated were quite compatible, with manual liquid-liquid extraction producing the highest PAH concentrations. It is worth noting that in the steam distillation extract, the "heavier" PAH, BP and OPP were not recovered as efficiently, in comparison with the other methods. Anthanthrene and coronene (molecular weights of 276 and 300, respectively) were both recovered by the steam distillation technique, but not nearly as efficiently as the "lighter" PAH.

TABLE 2

Steel Mill Process Stream Filtrate PAH Concentration in µg/L

Compound	Extraction Technique			
	Direct Aqueous Injection	liquid-liquid	continuous liquid-liquid	steam distillation
BkF	.08	.10	.11	.18
BaP	.23	.40	.29	.35
DBA	.03	.04	.03	.03
BP	.09	.12	.12	.03
OPP	.09	.13	.12	.05
5 PAH TOTAL	.52	.79	.67	.64

Detection Limit = .05 ng/L

A comparison of the extraction techniques was made between the filtered and non-filtered samples. The filtered samples comprised PAH associated with the particulate material, bottle and filter equipment washings, and the filtrate (dissolved PAH). These results are presented in Table 3. The variations in the filtered extraction procedures were small, in that the PAH concentrations from the particulate material and solvent washings were constant. The variation was due to the dissolved PAH extraction technique differences. There were substantial differences among the extraction methods for the non-filtered sample. Continuous liquid-liquid extraction gave the highest PAH concentration, while the liquid-liquid shake-out gave the lowest. There may have been slight variability in the non-filtered sample, because it was not possible to pool the entire sample as it was with the filtered sample. Concentrations of up to 470 µg/l of BaP had been detected in previous non-filtered samples of this process stream. Table 4 shows how the PAH are distributed in the sample.

3. STEEL MILL EFFLUENT

The steel mill process stream (flushing liquor) underwent the following treatment in the plant. The liquor passed through a tar decanter and a two-stage ammonia still; free and fixed ammonia were removed; and finally, the effluent was subjected to biotreatment. The effluent, at this stage, contained 600-1300 mg/l of suspended solids. A sample was collected at this point in the process and had a suspended solids value of 1140 mg/l. Filtration of the sample was extremely slow. Microscopic examination of the particulate material revealed fine particles ranging between 1-3 µm in size. A filter aid ("Celite") was used to assist filtration.

The concentration of the PAH in the filtrate was low. Extraction method comparisons of the dissolved PAH fraction are given in Table 5. The continuous liquid-liquid and steam distillation procedures recovered more PAH; however, there were no significant differences in efficiency among the

TABLE 4

Distribution of PAH in the
Steel Mill Process Stream

PAH associated with		
Particulate (>.45 μ)	Washings+	Filtrate*
63.1%	17.8%	19.1%

+ Bottle and filtration equipment

* Dissolved PAH is an average value for the 3
extraction methods evaluated

TABLE 5

Treated Steel Mill Effluent Filtrate PAH Concentration in ng/L

Compound	Extraction Technique		
	liquid-liquid	Continuous liquid-liquid	Steam distillation
BkF	.3	.5	.5
BaP	.4	.8	.9
DBA	nd	.1	.1
BP	.1	.3	.2
OPP	.1	.4	.3
5 PAH TOTAL	.9	2.1	2.0

Detection Limit = .05 ng/L

methods. Of the two procedures mentioned above, the steam distillation technique provided a "cleaner" extract as shown in Figure 2. In general, when working in the parts per trillion concentration range, the concentrated extracts were first subjected to a column chromatography clean-up, prior to analysis.

Comparing the PAH concentration from the filtered sample (particulate matter and filtrate) with PAH in the non-filtered sample, all extraction procedures yielded higher concentrations for the non-filtered sample. These results are presented in Table 6. Again, the variation in the PAH concentration from the extraction techniques of the filtered sample was small. The rationale is the same as stated previously.

The filtered sample PAH concentrations were lower possibly because extraction of the PAH from the particulate matter on the filters and filter aid may not have been complete. This was not surprising, considering the total surface area of particulate matter to which the PAH could be adsorbed. The PAH associated with the particulate fraction comprised 98.2% of the total PAH concentration. Perry (1) has discussed the effect of suspended solids upon PAH extraction efficiency.

The continuous liquid-liquid extraction of the non-filtered sample produced the highest PAH value, while the liquid-liquid shake-out produced the lowest. This was most likely because there was much longer solvent contact with the former extraction procedure than the latter.

The "cleanest" non-filtered extract was obtained from the steam distillation method. This is illustrated in Figure 3, which compares the continuous liquid-liquid and steam distillation extract chromatograms. The manual liquid-liquid extract chromatogram was similar to that of the continuous liquid-liquid extract chromatogram.

TABLE 6

Comparison of Total Filtered and Non-Filtered
PAH Concentrations from a Steel Mill Effluent in ng/L

Compound	Extraction Technique					
	liquid-liquid		Continuous liquid-liquid		Steam distillation	
	Filtered	Non-Filtered	Filtered	Non-Filtered	Filtered	Non-Filtered
BkF	15.3	20	15.5	25	15.5	30
BaP	42.4	62	42.8	75	42.9	78
DBA	4.7	6.5	4.8	10	4.8	10
BP	17.1	21	17.3	34	17.2	19
OPP	13.1	17	13.4	33	13.3	23
5 PAH TOTAL	92.6	127.5	93.8	177	93.7	160

Detection Limit = .05 ng/L

4. RECEIVING WATERS

The particular body of water sampled received discharges from two steel mills, a sewage treatment plant and a number of primary and secondary industries. Heavy marine traffic, plus atmospheric deposition also contributed to the PAH concentration in this water body. The sample was collected approximately 0.5 meters below the water surface. Sample filtration was relatively easy in that the suspended solids level was 10 mg/l. Microscopic examination of this material showed particles that were 5 μ m and larger. Numerous diatoms were observed.

The recovery of the dissolved PAH in the filtrate by the three extraction procedures is presented in Table 7. There was little difference in the recoveries among the three methods. Also, there was little difference between the PAH concentrations in the filtered and non-filtered sample (Table 8). This was probably due in part to the relatively low suspended solids value. As with the non-filtered effluent sample, the continuous liquid-liquid technique provided the highest PAH recovery. In the receiving waters, the PAH associated with the particulate matter was 85.6% of the total PAH concentration.

CONCLUSIONS

The micro adsorption column had serious drawbacks in that samples had to be filtered prior to concentration of the filtrate. A relatively expensive pumping system was needed, as pressures of greater than 35 kg/cm² (500 psi) were required at times. This method was the most time consuming and the micro adsorption columns were expensive.

The steam distillation extraction technique provided the cleanest extract as determined by HPLC. As expected, the higher molecular weight PAH, because of their relative lack of volatility, were not recovered as

TABLE 7

Receiving Water Filtrate PAH Concentration in ng/L

Compound	Extraction Technique		
	liquid-liquid	Continuous liquid-liquid	Steam distillation
BkF	.6	.5	.5
BaP	1.3	1.2	1.0
DBA	.4	.5	.4
BP	.8	.6	.5
OPP	.5	.1	.5
5 PAH TOTAL	3.6	2.9	2.9

Detection Limit = .05 ng/L

TABLE 8

Comparison of Total Filtered and Non-Filtered PAH
Concentrations from the Receiving Waters in ng/L

Compound	Extraction Method					
	liquid-liquid		Continuous liquid-liquid		Steam distillation	
	Filtered	Non-Filtered	Filtered	Non-Filtered	Filtered	Non-Filtered
BkF	3.6	3.8	3.5	6.3	3.5	4
BaP	7.3	7.3	7.2	12	7	9
DBA	1.0	1.0	1.1	1.2	1.0	1.1
BP	4.8	5.8	4.7	7.3	4.5	7.2
OPP	5.3	6.0	4.8	8.5	5.3	6
5 PAH TOTAL	22.0	23.9	21.3	35.3	21.3	27.3

Detection Limit = .05 ng/L

well as the lower molecular weight PAH. Recoveries of more water soluble heterocyclic PAH would probably be less effective applying this method. Heat labile compounds would also be affected by this method.

The liquid-liquid shake-out and the continuous liquid-liquid extraction are both EPA approved methods for the extraction of base-neutral priority pollutants. In the 3 sets of non-filtered samples, continuous liquid-liquid extraction recovered the most PAH, followed by the steam distillation, with the manual liquid-liquid extraction recovering the least PAH, by comparison. There were no significant differences among the methods for the 3 sets of filtered samples, primarily because the PAH associated with particles composed the bulk of the materials and was common to all extraction procedures.

In summary, the continuous liquid-liquid extraction technique is preferred over the liquid-liquid shake-out. There is some degree of subjectivity in the shake-out, specifically the effort put into the shaking, whereas, this variable does not exist with the other method. Moreover, this extraction procedure yields higher PAH values for the same sample.

If filtration of a sample is required, there is no basic difference in the dissolved PAH recoveries by the three methods. If filtration is not required, there are significant differences. The findings in this study indicate continuous liquid-liquid extraction to be the method of choice for PAH extraction of non-filtered samples.

REFERENCES

1. Acheson, M. A., Harrison, R. M., Perry, R., and Wellings, R. A.
(1975): Factors Affecting the Extraction and Analysis of Polynuclear Aromatic Hydrocarbons in Water. Water Research, 10: 207-212.
2. Lewars, E. G. (1979): Aldrichimica Acta, 12: 22.
3. Likens, S. T. and Nickerson, G. B. (1964): Proc. Am. Soc. Brew. Chem., 5.
4. Smillie, R. D., Wang, D. T., and Meresz, O. (1978): The Use of a Combination of Ultraviolet and Fluorescence Detectors for the Selective Detection and Quantitation of Polynuclear Aromatic Hydrocarbons by High Pressure Liquid Chromatography. J. Environ. Sci. Health, A13: 47-59.
5. Veith, G. D. and Kimus, D. M. (1977): An Exhaustive Steam-Distillation and Solvent-Extraction Unit for Pesticides and Industrial Chemicals. Bull. Environ. Contamin. and Tox., 17: 631-636.

Figure 1. Fluorescence high pressure liquid chromatogram of a 10 μ l direct aqueous injection of a filtered steel mill process stream sample.

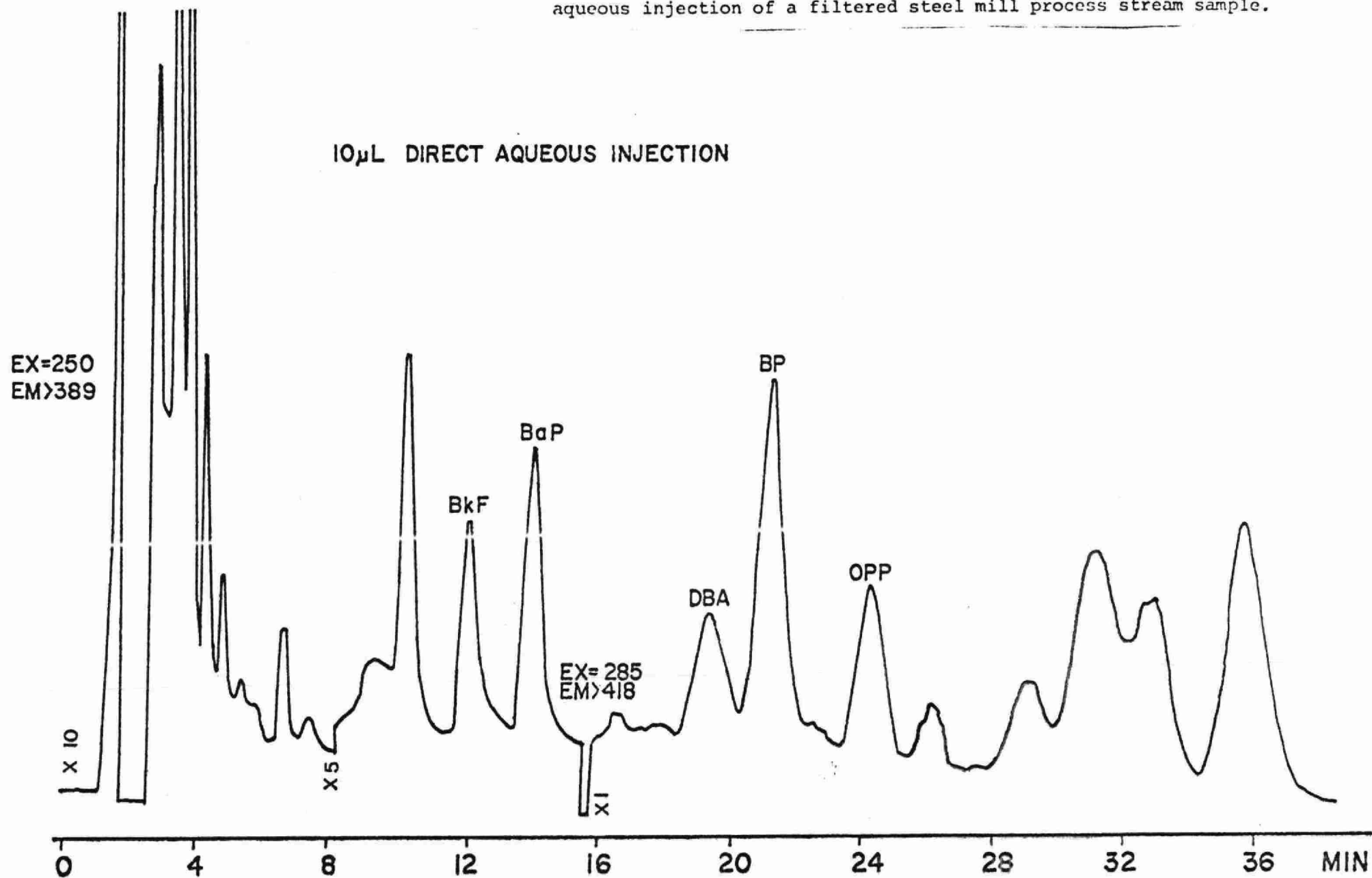


Figure 2. Comparison of chromatograms of steel mill effluent filtrate extracts from continuous liquid-liquid extraction, with and without clean-up, and steam distillation extraction.

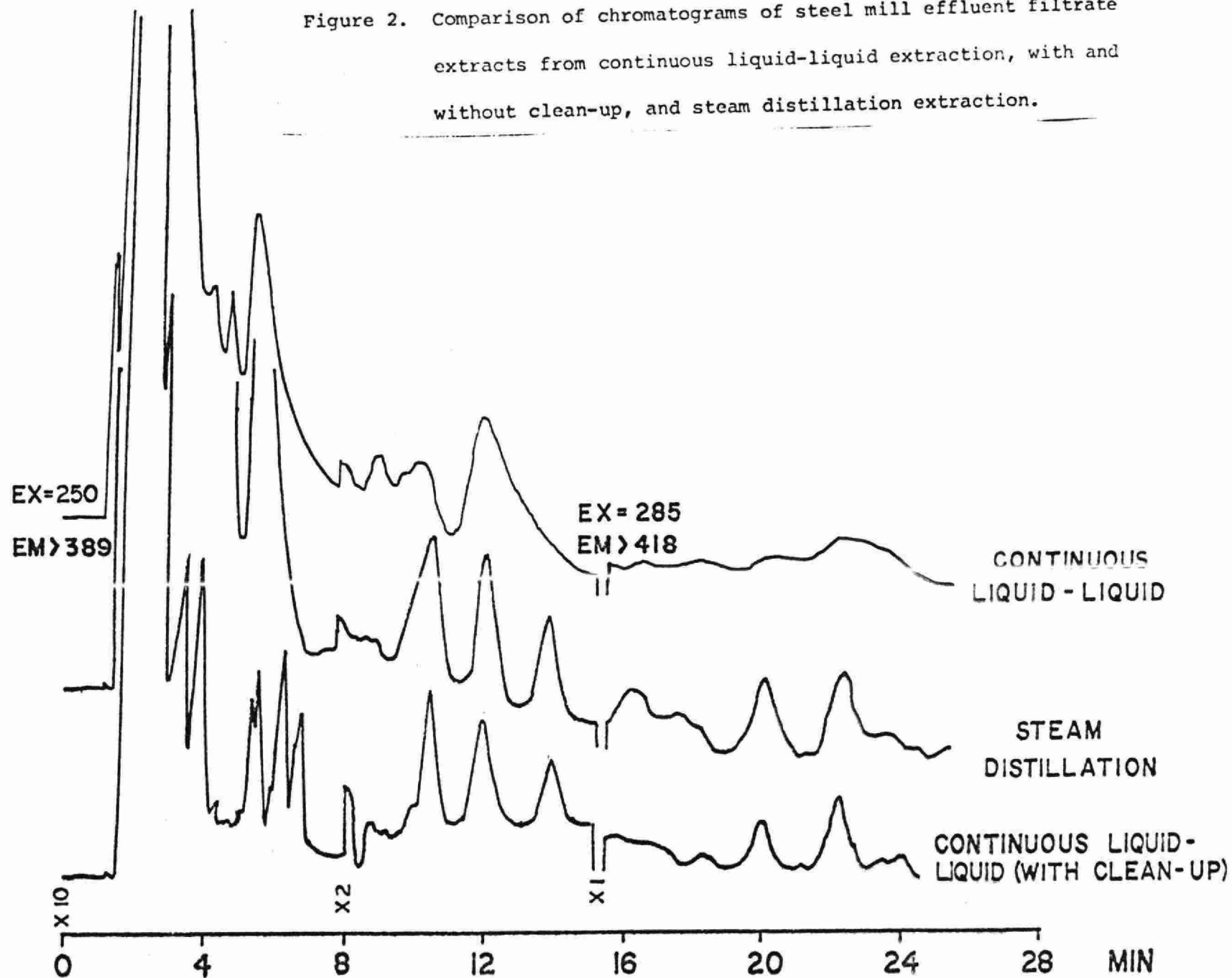


Figure 3. Comparison of chromatograms of non-filtered steel mill effluent extractions obtained by continuous liquid-liquid and steam distillation extraction techniques.

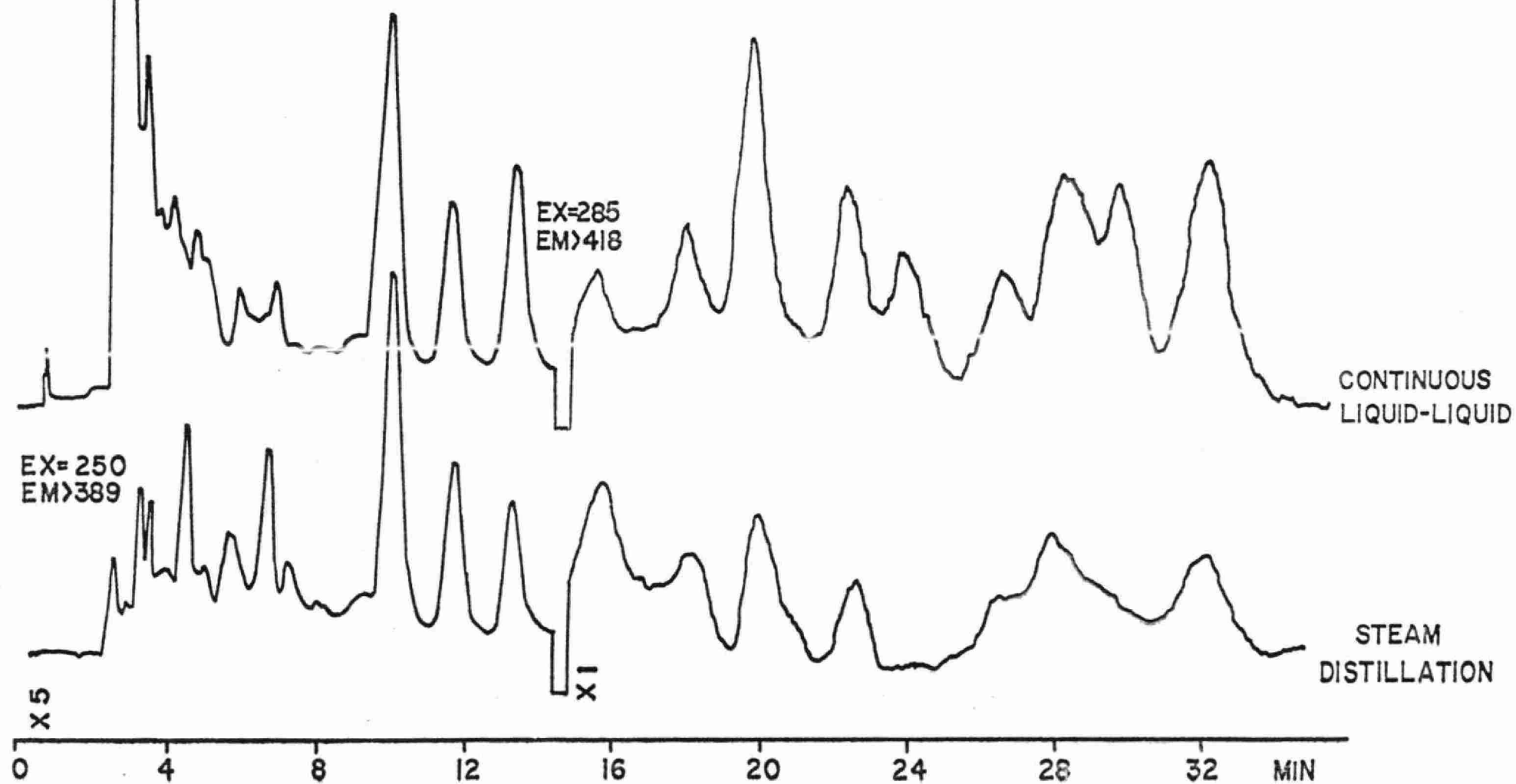


TABLE 3

Comparison of Total Filtered and Non-Filtered
PAH Concentrations from a Steel Mill Process Stream in $\mu\text{g/L}$

Compound	Extraction Technique						
	Direct Aqueous Injection	liquid-liquid		continuous liquid-liquid		steam distillation	
	Filtered	Filtered	Non-Filtered	Filtered	Non-Filtered	Filtered	Non-Filtered
BkF	.52	.54	.23	.55	.70	.62	.50
BaP	1.56	1.73	.72	1.62	2.30	1.68	1.10
DBA	.18	.19	.10	.18	.38	.18	.08
BP	.56	.59	.33	.59	1.08	.50	.13
OPP	.63	.67	.35	.66	1.05	.59	.26
5 PAH TOTAL	3.45	3.72	1.73	3.60	5.51	3.57	2.07

Detection Limit = .05 ng/L



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